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Organocatalytic synthesis of new telechelic polycarbonates and study of their chemical reactivity



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ABSTRACT

A two-step versatile process for telechelic polycarbonates synthesis is described. 1-*n*-butyl-3methylimidazolium-2-carboxylate (BMIM-2-CO₂) was used as thermolabile precursor of *N*-heterocyclic carbene (NHC) organocatalyst. In a first step, synthesized branched fatty diols or commercially available linear diols were reacted with an excess of dimethylcarbonate (DMC) to afford oligocarbonates with methylcarbonate end-groups. Then, the methylcarbonate groups were reacted with hydroxyl groups of 9-decen-1-ol, 4-hexyn-1-ol and 4-hydroxybenzene ethanol leading to telechelic oligomers with alkene, alkyne and phenol functionalities. Reactivity of these end-groups towards polymerization was successfully evidenced. This procedure could be used for preparing a range of new telechelic oligocarbonates. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Polycarbonates (PCs) are a class of very important materials for human life. They are used as engineering plastics thanks to many properties such as transparency, toughness, biodegradability, biocompatibility, thermal stability and mechanical durability.

Aliphatic PCs can be prepared through three pathways: (i) ring opening polymerization of cyclic carbonates, (ii) copolymerization of epoxides with carbon dioxide and (iii) polycondensation. In the industry, PCs are still produced by polycondensation between alkanediols and phosgene derivatives exhibiting toxological effetcs. In this respect, the development of green and straightforward processes for PCs elaboration is a subject of great interest and is still under investigations [1]. Recently, aliphatic PCs have been synthesized using dimethyl carbonate (DMC) as carbonyl source instead of phosgene. DMC is an Eco-friendly product thanks to its biodegradability and low toxicity (1000 times less than phosgene) [2]. Naik et al. [3] have obtained polycarbonates by reacting DMC from diols containing 3 to 6 carbons in presence of 1-n-butyl-3methylimidazolium-2-carboxylate (BMIM-2-CO₂) as metal-free pre-catalyst. Decarboxyaltion of BMIM-2-CO₂ induced by heating lead to the formation of an N-heterocyclic carbene (NHC) which is the catalytic active species [3-7]. 1,5,7-triazabicyclo[4,4,0]dec-5ene (TBD) was also used as an organocatalyst for the polycondensation of diol and DMC [8]. Furthermore, polycarbonate synthesis can be conducted by carbonate metathesis polymerization using K₂CO₃ as catalyst [9].

Polymers are called "telechelic" when they contain two reactive functional groups at their chain-ends. They are usually used for synthesis of block copolymers and polymeric networks [10,11]. They also can be employed as linkers to modify properties of other materials [12]. Few examples of telechelic polycarbonate synthesis have been described in the literature. In 1994, α , ω -tertiary amino and α , ω -quaternary ammonium polycarbonates have been synthesized from bisphenol A and phosgene [13]. The functionalization of the chain-ends was achieved with *N*,*N*'-dimethylaminophenol and iodoammonium derivatives as chain limiters. Few years later, Korn et al. [14] have prepared telechelic oligomers by depolymerization of commercial bisphenol A polycarbonates in presence of different diaryl carbonates (diphenylcarbonate, di-2-naphthyl carbonate, di-2-Allylphenyl carbonate and di-4-carbonitrile-4-biphenyl carbonate) and tBuOK as catalyst.

Most of the prepared telechelic polycarbonates bear hydroxy end-groups and are known as bis(hydroxy) polycarbonates (BHP). They can be obtained by copolymerization of cyclohexene oxide and carbon dioxide in presence of zinc catalyst [15], *via* polycondensation of bisphenol A and diphenyl carbonate using lanthanum catalyst [16], or also by ring opening polymerization



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(ROP) of trimethylene carbonate (TMC) with zinc catalyst in presence of a diol [17,18]. Moreover, BHP can lead to a bifunctional chloro-telechelic polycarbonate (BCP) by esterification with α chlorophenylacetyl chloride [16]. BHP and BCP are then used for synthesis of triblock copolymers: PS-PC-PS and PMMA-PC-PMMA by ATRP [16], or PLA-PC-PLA by reaction with lactide [15]. On the other hand, α , ω -di-(cyclic carbonate) polycarbonate have been prepared by Helou et al. [19] in three steps while Colonna et al. [20] synthesized telechelic sulfonated polycarbonate ionomers by melt polycondensation.

In this work, we describe a versatile two-step organocatalytic synthesis of telechelic PCs bearing novel functionalities. In a first step, methylcarbonate-ended PCs were synthesized from several diols and an excess of DMC, in presence of BMIM-2-CO₂ as catalyst. Then, the methylcarbonate end-groups were reacted with hydroxyl functionalized compounds bearing several chemical groups to afford PCs with alkyne, alkene and phenol end-groups. The reactivity of these groups towards polymerization was also studied (Fig. 1).

2. Experimental section

2.1. Materials

Anhydrous dimethylcarbonate (\geq 99%), 1,12-dodecanediol (99%), 9-decen-1-ol (97%), (1,3-*bis*-(2,4,6-trimethylphenyl)-2imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene) ruthenium (Hoveyda-Grubbs catalyst 2nd generation, 97%), dibutyltindilaurate (95%), ethyl vinylether (99%), sodium ascorbate (\geq 98%) and copper sulphate pentahydrate (99.9%) were purchased from Sigma Aldrich (France). 4-pentyn-1-ol (98%) and *p*-phenylene diisothiocyanate (98%) were obtained from Alfa Aesar (France). 4-hydroxybenzene ethanol (98%) was provided from Acros (France) and benzoquinone (100%) from Merck (France).

2.2. Instruments

NMR spectra were recorded on a Bruker Avance (300 MHz) Spectrometer. IR spectra were recorded on a FTIR (Perkin–Elmer) equipped with a diamond ATR device (attenuated total reflection). Molecular weights and molecular weight distributions were measured using size exclusion chromatography (SEC) on a Varian PL-GPC50 device equipped with two mixed packed columns (PL gel mixed type C). Dichloromethane was used as eluent at a flow rate of 1 mL min⁻¹ at 25 °C and polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) was carried out on a DSC Q2000 apparatus (TA Instruments). Samples were heated from -90 °C to 100 °C under nitrogen using a heating rate of 10 °C/ min. TGA measurements were performed on a TGA Q500 system (TA Instruments) under nitrogen atmosphere. Samples were heated from 30 °C to 500 °C using a rate of 10 °C/min.

2.3. Synthesis of BMIM-2-CO₂

Catalyst was synthesized according to the procedure described in literature [3]. 2.90 mL (22 mmol) of 1-*n*-butylimidazole, 4 mL



Fig. 1. Versatile approach for synthesis of new telechelic polycarbonates and their polymers.

(47.5 mmol) of dimethyl carbonate (DMC) and 25 mL of methanol were introduced in a Schlenk tube under argon atmosphere. The mixture was transferred *via* cannula to a 70 mL stainless steel batch reactor previously purged under argon. The mixture was stirred and heated to 135 °C for 7 h. The mixture was then transferred into a flask and methanol was evaporated under vacuum (trap-to-trap distillation). The pale yellow viscous residue obtained was washed with 4 × 20 mL of dry diethyl ether. The obtained solid was dried overnight under vacuum to give pure BMIM-2-CO₂ as a white powder in 66% yield. ¹H NMR (D₂O, 300 MHz, δ /ppm): 0.85 (m, 3H, CH₃-CH₂), 1.23 (m, 2H, CH₃-CH₂), 1.75 (m, 2H, CH₃-CH₂-CH₂), 3.89 (s, 3H, N-CH₃), 4.33 (m, 2H, N-CH₂), 7.32 (d, 1H, J = 2.0 Hz, CH=CH-N-CH₃), 7.37 (d, 1H, J = 2.0 Hz, CH=CH-N-CH₃). ¹³C NMR (D₂O, 75 MHz, δ /ppm): 13.0, 19.2, 32.3, 36.8, 49.7, 122.1, 123.5, 140.3, 158.8.

2.3.1. Preparation of (9Z)-9-octadecene-1,12-diol (diol 1) [21]

To a solution of lithium aluminohydride (1.83 g, 48.1 mmol) in 75 mL of anhydrous diethyl ether, in a two-necked round bottom flask with magnetic stirring under nitrogen atmosphere, methyl ricinoleate (9.6 mmol) in 50 mL of anhydrous diethyl ether was added. After stirring for 6 h at room temperature, hydrolysis of lithioaluminate complexes was performed by dropwise addition of water. The reaction mixture was washed with saturated aqueous NaCl and dried over MgSO₄. The solvent was then evaporated to afford (9Z)-9-Octadecene-1,12-diol (yield: 81%). ¹H NMR (300 MHz, $CDCl_3, \delta/ppm$): 0.86 (t, 3H, J = 7.15 Hz, CH₃), 1.30 (m, 18H, CH₂), 1.45 (m, 2H; $CH_2-CH_2-CH(R)-OH$), 1.55 (t, 2H,] = 6.78 Hz; CH_2 - CH_2 -OH), 2.04 (q, 2H, J = 7.15 Hz; CH_2 - CH_2 -CH =), 2.20 (t, 2H, I = 6.4 Hz; =CH-CH₂-CH(R)-OH), 3.63 (m, 3H; CH-OH and *CH*₂–OH), 5.4 (m, 1H; *CH*=CH), 5.59 (m, 1H; *CH*=*CH*). ¹³C NMR (75 MHz, CDCl₃, δ/ppm): 13.2, 21.7, 24.8, 26.5, 28.3–28.7, 30.9, 31.8, 34.4, 35.9, 62.0, 70.6, 124.3, 132.5. IR (ATR): $v = 3327 \text{ cm}^{-1}(\text{s}, v_{\text{OH}})$, disappearance of ester band at 1736 cm⁻¹.

2.4. Preparation of fatty diol from methyloleate (diol 2)

To a solution of methyloleate (17.7 mmol) in 100 mL of dichloromethane, in an erlenmeyer with magnetic stirring at 0 °C, were added *m*-chloroperoxybenzoic acide (*m*-CPBA, 26.6 mmol). After stirring for 3 h at 0 °C, the reaction mixture was washed with water and this aqueous phase was extracted with dichloromethane. All organic phases were washed with warm water and dried (MgSO₄). The solvent was evaporated to afford epoxidized methyloleate in 90-95 % yield. To a solution of lithium aluminohydride (1.83 g, 48.1 mmol) in 75 mL of anhydrous diethyl ether, in a twonecked round bottom flask with magnetic stirring under nitrogen atmosphere, epoxidized methyl oleate (9.6 mmol) in 50 mL of anhydrous diethyl ether was added. After stirring for 6 h at room temperature, hydrolysis of lithioaluminate complexes was performed by dropwise addition of water. The reaction mixture was washed with saturated aqueous NaCl and dried (MgSO₄). The solvent was evaporated to afford the fatty diol in 80-85% yields. ¹H NMR (300 MHz, CDCl₃, δ /ppm): 0.88 (s, 3H, J = 6.72 Hz, CH₃); 1.24-1.59 (m, 30H, alkyl chain); 3.58 (m, 1H, CH-OH); 3.64 (m, 2H, CH₂-OH). ¹³C NMR (75 MHz, CDCl₃, δ/ppm): 13.2, 21.8, 25.3, 26.0, 28.4–28.9, 31.0, 32.8, 37.1, 62.2, 71.2. IR (ATR): $v = 3338 \text{ cm}^{-1}(\text{s}, \text{s})$ v_{OH}), disappearance of ester band at 1740 cm⁻¹.

2.5. Preparation of 1,12-diazidododecane

In a two-necked round bottom flask equipped with a magnetic stirring and a nitrogen flow, 6.0 mL of Et_3N (45.5 mmol) followed by 3.9 mL (50.0 mmol) of mesyl chloride were added in a dropwise manner to a solution of dodecane-1,12-diol (22.7 mmol) in 50 mL of

diethyl ether. After stirring for 1 h at room temperature, the reaction mixture was washed with water and dried over MgSO₄. The solvent was then evaporated to afford 1,12-dimesyl-dodecane in 90–93% yields. Then, to a solution of 1,12-dimesyl-dodecane (61 mmol of mesylate groups) in 140 mL of DMF, was added NaN₃ (91.5 mmol). After stirring for 24 h at 75 °C, the reaction mixture was washed with 50 mL of water, extracted with diethyl ether (6 × 50 mL) and dried over MgSO₄. The solvent was then evaporated to afford 1,12-diazido-dodecane in 88–90% yields. ¹H NMR (300 MHz, CDCl₃, δ /ppm): 1.26–1.61 (m, 20H, CH₂), 3.25 (t, 4H, CH₂–N₃). ¹³C NMR (75 MHz, CDCl₃, δ /ppm): 25.1; 25.7; 27.8, 28.5, 30.7, 51.4. IR: ν = 2091 cm⁻¹ (s, ν N₃).

2.6. Polymers synthesis

2.6.1. General procedure for synthesis of methyl carbonate terminated PCs

Under argon atmosphere, 1,12-dodecanediol (1.0 g, 5.02 mmol), DMC (1.8 mL, 21.34 mmol) and 5 mol% of 1-*n*-butyl-3-methylimidazolium-2-carboxylate (0.045 g, 0.2511 mmol) were placed in a dried Schlenk tube equipped with a magnetic stirrer. The reaction mixture was heated under stirring for 15 min at 100 °C. The flask was then immersed in a heated oil bath at 150 °C for 6 h under vacuum, to carry out the polymerization. For linear PCs (PC3-MC and PC4-MC), the reaction mixture was cooled and the residue was purified by dissolving in THF and precipitating with ethanol (yields: 85 and 80, respectively). The polymer was isolated by filtration and dried under vacuum. Branched fatty PCs (PC1-MC and PC2-MC) were viscous liquids and could not be precipitated.

Characterizations of PC1-MC: ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 0.86 (t, n × 3H, J = 6.9 Hz, CH₃-CH₂), 1.28 (m, n × 18H, alkyl chain), 1.56–1.67 (m, n × 4H, CH₂–CH–O–C=O, CH₂–CH₂–O–C=O), 2.01 $(q, n \times 2H, J = 6.7 \text{ Hz}, CH = CH - CH_2 - CH_2), \overline{2.32} (d-d, n \times 2H, J = 6.$ Hz, J = 8.7 Hz, CH-CH₂-CH=CH), 3.75 (s, 3H, CH₂-O-C(=O)- $O-CH_3$), 3.76 (s, 3H, CH-O-C(=0)-O-CH_3), 4.10 (t, n × 2H, J = 6.7 Hz, $CH_2-O-C=O$), 4.68 (q, n × 1H, J = 6.2 Hz, CH-O-C=O), 5.43–5.52 (\overline{m} , n × 2H, HC=CH). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 14.0, 22.5-33.7, 67.8, 67.9, 78.2, 123.7, 132.9, 155.1. IR (ATR): $v = 1735 \text{ cm}^{-1}$ (s, $v_{carbonate}$), 1445 cm⁻¹ (m, $v_{methyl carbonate end-goups}$). *Characterizations of PC2-MC*: ¹H NMR (CDCl₃, 300 MHz, δ/ppm): 0.87 (t, $n \times 3H$, J = 6.5 Hz, $CH_3 - CH_2$), 1.25 (m, $n \times 24H$, alkyl chain), 1.55–1.65 (m, n × 6H, CH₂–CH–O–C=O, CH₂–CH₂–O–C=O), 3.76 (s, 6H, $CH_2-O-C(=O)-O-CH_3$, $CH-O-C(=O)-O-CH_3$), 4.10 (t, $n \times 2H$, J = 6.5 Hz, CH₂-O-C=O), 4.67 (q, $n \times 1H$, J = 5.6 Hz, CH-O-C=O). ¹³C NMR (CDCl₃, 75 MHz, δ/ppm): 14.1, 22.7-34.0, 68.0, 78.1, 155.3. IR (ATR): $v = 1735 \text{ cm}^{-1}$ (s, $v_{\text{carbonate}}$), 1445 cm^{-1} (m, $\nu_{methyl\ carbonate\ end\ goups}).$

Characterizations of PC3-MC: ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, $n \times 12$ H, alkyl chain), 1.64 (q, $n \times 4$ H, J = 7.2 Hz, CH₂-CH₂-O), 3.75 (s, 6H, O-CH₃), 4.11 (t, $n \times 4$ H, J = 6.7 Hz, CH₂-O).¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 25.6, 28.6, 29.1, 29.4, 54.6, 68.0, 68.2, 155.4, 155.9. IR (ATR): v = 1735 cm⁻¹ (s, $v_{carbonate}$), 1445 cm⁻¹ (m, v_{methyl} carbonate end-goups). Characterizations of PC4-MC: ¹H NMR (CDCl₃, 300 MHz, δ /ppm):

Characterizations of PC4-MC: ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, $n \times 16$ H, alkyl chain), 1.65 (q, $n \times 4$ H, J = 7.0 Hz, CH₂-CH₂-O), 3.77 (s, 6H, O-CH₃), 4.11 (t, $n \times 4$ H, J = 6.7 Hz, CH₂-O).¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 24.8, 27.8, 28.3, 28.6, 53.7, 67.1, 67.3154.6, 155.0. IR (ATR): $\nu = 1735$ cm⁻¹ (s, $\nu_{carbonate}$), 1445 cm⁻¹ (m, ν_{methyl} carbonate end-goups).

2.6.2. General procedure for chain-ends functionalization

Under argon atmosphere, methylcarbonate terminated PC (0.5 g, 0.278 mmol), 9-decenen-1-ol or 4-hexyn-1-ol or 4-hydroxybenzene ethanol (3 eq, 0.833 mmol) and 5 mol% of 1-*n*-butyl-3-methylimidazolium-2-carboxylate (4.0 mg, 0.0139 mmol)

were placed in a dried Schlenk tube equipped with a magnetic stirrer. The reaction mixture was heated under stirring for 15 min at 100 °C. The flask was then immersed in a heated oil bath at 150 °C for 6 h under vacuum. Then, the reaction mixture was cooled and the residue was purified by dissolving in THF and precipitating with ethanol. The polymer was isolated by filtration and dried under vacuum.

Characterizations of PC4-alkene: (yield: 84%) ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, $n \times 16H+8H$, alkyl chain), 1.65 (q, $n \times 4H$, J = 6.9 Hz, CH₂-CH₂-O), 2.03 (q, 4H, J = 6.18 Hz, CH₂-CH= CH₂), 3.71 (t, 4H, J = 6.7 Hz, O-CH₂ end-groups), 4.11 (t, $n \times 4H$, J = 6.6 Hz, O-CH₂), 4.95 (d-d, 4H, J = 20.3 and J = 11.4 Hz, CH= CH₂), 5.80 (m, 2H, CH=CH₂). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 24.8, 27.8, 27.9, 28.1, 28.3, 28.6, 28.6, 31.9, 32.9, 52.5, 67.1, 113.2, 138.2, 154.5. IR (ATR): Disappearance of the band of the methyl carbonate end-groups at 1445 cm⁻¹.

Characterizations of PC4-phenol: (yield: 88%) ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, $n \times 16$ H, alkyl chain), 1.66 (q, $n \times 4$ H, J = 7.1 Hz, CH₂-CH₂-O), 2.90 (t, 4H, J = 7.2 Hz, CH₂-Ph), 4.11 (t, $n \times 4$ H, J = 6.7 Hz, O-CH₂), 4.28 (t, 4H, J = 7.2 Hz, O-CH₂-CH₂-Ph), 6.78 (m, 4H, aromatics CH=C(OH)-CH), 7.1 (m, 4H, aromatics CH=C(OH)-CH=C(OH)-CH=C(OH)-CH=C). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 24.8, 27.8, 28.3, 28.5, 28.6, 33.4, 67.1, 114.5, 129.2, 154.6. IR (ATR): aromatic bands between 1500 and 1600 cm⁻¹, disappearance of the band of the methyl carbonate end-groups at 1445 cm⁻¹.

Characterizations of PC4-alkyne: (yield: 95%) ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, $n \times 16H+8H$, alkyl chain), 1.65 (q, $n \times 4H$, J = 6.9 Hz, CH₂–CH₂–O), 3.65 (t, 4H, J = 6.7 Hz, O–CH₂ chain-ends), 4.11 (t, $n \times 4H$, J = 6.6 Hz, O–CH₂). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 24.8, 27.8, 28.3, 28.6, 28.6, 67.1, 154.5. IR (ATR): Disappearance of the band of the methyl carbonate end-groups at 1445 cm⁻¹.

2.6.3. Reactivity study of alkene ends groups by ADMET polymerization

Metathesis was carried out as described by Firdaus and Meier [23]. Alkene terminated polycarbonate (PC4-alkene) (0.4 g, $1.36 \cdot 10^{-4}$ mol) and 1,4-benzoquinone (2 mol%) were introduced in a round bottom flask equipped with a magnetic stirrer. The mixture was stirred 5 min at 80 °C. Then, (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene) ruthenium (Hoveyda-Grubbs catalyst 2nd generation) was added. The reaction was carried out at 80 °C under vacuum. After 4 h, the mixture was dissolved in THF and an excess of ethyl vinyl ether was used to quench the reaction. ADMET Polymer was purified by precipitation in ethanol and filtration (yield: 87%). ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 1.26 (m, 16H+8H, alkyl chain), 1.64 (q, 4H, J = 6.9 Hz, CH₂-CH₂-O), 1.96 (m, mx4H, CH₂-CH=CH), 3.63 (t, 4H, J = 0-CH₂), 4.11 (t, 4H, J = 6.7 Hz, 0-CH₂), 5.37 (m, 2H, CH=CH). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 24.8, 27.8, 28.3, 28.6, 28.6, 31.9, 67.1, 154.5. IR (ATR): ν = 1735 cm⁻¹ (s, $\nu_{carbonate}$).

2.7. Reactivity study of phenol end-groups towards diisothiocyanates

Phenol terminated polycarbonate (PC4-phenol) was dissolved in THF (1 g mL⁻¹). The catalyst (DBTL) was added to the solutions in a ratio of [DBTL]/[OH] = 0.05. Then, *p*-phenylene diisothiocyanate was added in last with an effective ratio of [NCS]/[OH] = 1.05. The different solutions were cast in PTFE moulds under dried argon atmosphere for 2 h. The films formed (Poly(thio-urethane)) after solvent evaporation were cured for 22 h at 60 °C (yield: 100%). IR (ATR): $v = 3447 \text{ cm}^{-1}$ (w, v_{NH}), $v = 1736 \text{ cm}^{-1}$ (s, $v_{carbonate}$ and $v_{thiocarbamate}$), aromatic bands between 1500 and 1600 cm⁻¹ (w,

 $v_{C=C}$) and between 800 and 900 cm⁻¹ (w, γ_{C-H}), disappearance of isothiocyanate band at 2090 cm⁻¹.

2.8. Reactivity study of alkyne end-groups towards click cycloaddition with diazide

In a round bottom flask, alkyne terminated polycarbonate (PC4alkyne) (0.4 g, 2.10^{-5} mol) and 1,12-diazidododecane (1.1 eq) were dissolved in 24 mL of THF at 50 °C. After, 0.05 eq of CuSO₄ and 0.02 eq of sodium ascorbate were added. Then, the polymerization reaction was conducted at 50 °C for 24 h, under magnetic stirring. The polymer started to precipitate in the medium after only 4 h of reaction. Finally, HDC Polymer was recovered by filtration and dried under vacuum (yield: 90%). IR (ATR): v = 1736 cm⁻¹ (s, v_{carbonate}), disappearance of azide band at 2100 cm⁻¹.

3. Results and discussions

3.1. Synthesis and properties of methylcarbonate telechelic polycarbonate

Methylcarbonate terminated polycarbonates were prepared by polycondensation reaction of an excess of DMC with a diol in presence of BMIM-2-CO₂ as a metal-free catalyst. The use of this kind of catalyst in polymerization processes especially for medical application (where metal atoms can be forbidden in the future) is of great interest [24]. Several branched (1 and 2) and linear (3 and 4) diols were tested. 1,10-decanediol (3) and 1,12-dodecanediol (4) are commercially available diols. (9Z)-9-Octadecene-1,12-diol (1) was obtained by reduction of methyl ricinoleate with LiAlH₄. The second fatty diol (2) was obtained by epoxidation of the double bond of methyl oleate followed by reduction of both epoxide and ester groups with LiAlH₄. The product is statistically a mixture of octadecane-1,9-diol and octadecane-1,10-diol.

As described by Naik et al. [3], the polymerization reaction occurs according to a two-stage procedure. Firstly, the reaction medium was heated to 100 °C during t_1 minutes to allow the *in-situ* formation of the NHC active species by decarboxylation of BMIM-2-CO₂. Then, the polycondensation reaction (based on a transesterification process) was performed at 150 °C during t_2 hours under vaccum. These conditions favour the continuous elimination of the formed methanol. However, because of the volatility of DMC in these operating conditions, the use of a large excess of DMC was necessary to get methylcarbonate end-groups. Thus, a similar mechanism to that suggested in the past by Naik et al. [3], is also expected.

In order to use same polymerization conditions for all the chosen diols, and because the presence of secondary alcohol in the branched diols suggesting a lower reactivity, the reaction parameters were optimized using the branched diol **1** (Supporting Data). It was found that the optimal conditions leading to a total conversion of alcohol groups into methyl carbonate groups and to homogeneous SEC chromatogram with dispersity Đ close to 2 are the following:

- molar percentage of BMIM-2-CO₂: 5%;
- excess of DMC: 4.5 eq;
- time of catalyst activation at 100 °C (t₁): 15 min;
- reaction time at 150 °C (t_2): 6 h.

FTIR analysis of the obtained PCs showed mainly the presence of the carbonyl band of carbonate function at around 1736 cm⁻¹ and a characteristic band of methyl carbonate end groups at 1445 cm⁻¹. The FTIR spectrum of PC4-MC is shown in Fig. 2 as a typical example.



Fig. 2. Selected zones of the FTIR spectra of the prepared telechelic PCs.

The NMR analysis showed a total conversion of the alcohol groups into carbonate groups. The ¹H NMR spectrum of PC4-MC is depicted in Fig. 3. Therefore, we can assume that all PC chains contain two carbonate end-groups (conversion: p = 1). Thus, the absolute values of the polymerization degree (\overline{Pn}) and average molecular weight (\overline{Mn}) of the prepared polycarbonates were calculated from ¹H NMR spectra (Table 1) as follows:

$$\overline{Pn} = \frac{I_{CH_2O} \times x}{y \times I_{chain-ends}}$$
(1)

$$\overline{Mn} = M_{chain-ends} + M_{repeating unit} \times \overline{Pn}$$
(2)

where:

- *M*_{chain-ends} is the molecular weight of the chain-ends.
- *M_{repeating unit}* is the molecular weight of the polymer repeating unit.
- I_{CH2O} is the relative integrations of the peaks arising from protons in α position to the oxygen of the carbonate linkage (around 4.10 ppm); y: is the number of theses protons.
- *I*_{chain-ends} is the relative integration of protons of the end-groups;
 x: is the number of these protons.

Using the Carothers equation (with p = 1), we can also calculate the effective stoechiometric coefficient of DMC (1/r) used during the polymerization process, as follows (Table 1):

$$\frac{1}{r} = \frac{\overline{Pn} + 1}{\overline{Pn} - 1}$$
(3)

Molecular weights (\overline{Mn} and \overline{Mw}) and dispersity (\oplus) were also determined by SEC, using polystyrene (PS) standard calibration, and are depicted in Table 1.

One can observe that 1/r values were comprised between 1.10 and 1.31, which is far from the started DMC stoechiometric coefficient of 4.50 (Table 1). Absolute \overline{Mn} values were comprised between 1100 and 6900 g/mol. The methylcarbonate terminated PCs based on saturated and unsaturated fatty diols (PC1-MC and PC2-MC) exhibited lower 1/r values and higher \overline{Pn} and \overline{Mn} values comparing to the PCs based on 1,10-decanediol (PC3-MC) and 1,12-dodecanediol (PC4-MC). Furthermore, the branched biobased PCs being viscous liquids, they could not be precipitated, which explains their larger dispersity ($\overline{D} \ge 2.0$) in comparison with the precipitated linear PCs ($\overline{D} \sim 1.3$).



Fig. 3. ¹H NMR spectra of PC4-MC, PC4-alkene and ADMET polymer.

Table 1 Physico-chemical properties of the prepared telechelic PCs.

	Diol	End-groups	¹ H NMR			SEC		TGA		DSC ^c				
			Pn	1/r ^d	Mn	Mn	Ð	T _{5%} (°C)	T_{max} (°C)	$T_g(^{\circ}C)$	$T_m (^{\circ}C)$	$\Delta H_m (J/g)$	$T_c (°C)$	$\Delta H_{c} \left(J/g \right)$
PC1-MC	1	Methyl arbonate	22	1.10	6900	5300	2.0	278	317	-68	1	1	1	1
PC2-MC	2	Methyl carbonate	18	1.12	5700	3800	2.9	278	322	-52	-9	24	-18	22
PC3-MC	3	Methyl carbonate	5	1.50	1100	2500	1.6	1	1	1	30 (45)	108	16 (30)	104
PC4-MC	4	Methyl carbonate	7	1.31	1800	3300	1.3	266	373	1	60	119	51	114
PC4-MC control ^a	4	Methyl carbonate	10	1.21	2500	4500	1.7	1	1	, I	1	1	1	1
PC4-alkene	4	Alkene	9	1.25	2400	4500	1.3	284	374	,	60	123	51	114
PC4-phenol	4	Phenol	18	1.11	4500	8900	1.7	326	373	1	65	88	53	88
PC4-alkyne	4	Alkyne	52 ^b	1.04	12000 ^b	23,100	2.0	328	374	1	68	83	54	88

^a Conditions of the second step applied in absence of functional molecules.

^b Calculated using Benoit factor and not from the NMR spectrum because of very weak signals of the chain-end protons.

^c Data from second cycle.

^d 1/r is the calculated effective stoechiometric coefficient of DMC monomer towards diol monomer.

Thermal gravimetric analysis (TGA) of methylcarbonate terminated PCs revealed that all these polymers possess a good thermal stability up to 200 °C, with T_{5%} ranging from 266 to 278 °C and T_{max} ranging from 317 to 373 °C (Table 1). The TGA thermogram of PC4-MC is shown in Fig. 4 as example. DSC results revealed that polycarbonate based on unsaturated branched fatty diol (PC1-MC) was totally amorphous with $T_g = -68$ °C. On the other hand, PC2-MC, based on saturated branched fatty diol, exhibited a semicrystalline behaviour with Tg of -52° and T_m of -9 $^\circ\text{C}.$ These negative values can be explained by a plasticizing effect of the side chains, which increase the free volume. Furthermore, the presence of both of carbon-carbon double bond and hexyl side chain in PC1-MC disturbed polymer chain organization leading to absence of crystalline domains. This phenomenon has already been observed in the case of polyurethane [22] and polyamide [21] materials based on (9Z)-9-Octadecene-1,12-diol (diol 1) or its corresponding diamine. On the other hand, the linear PC3-MC and PC4-MC were also semi-crystalline with T_m values of 30 (second peak at 45 °C) and 60 °C, respectively; however, their Tg were not observed.

3.2. Synthesis and properties of alkyne, alkene and phenol telechelic polycarbonate

The introduction of new functionalities through chain-end chemical modifications was achieved on PC4-MC (based on 1,12-dodecanediol), used as representative polymer. This methylcarbonate terminated PC was reacted with an optimized excess (3 eq) of 9-decen-1-ol, 4-hexyn-1-ol or 4-hydroxybenzene ethanol, in presence of BMIM-2-CO₂ as catalyst (5%mol). The new telechelic polycarbonates were obtained after heating at 100 °C during 15 min and then at 150 °C for 6 h under vacuum.

It is noteworthy that the addition of these functional molecules as chain limiter to the starting mixture of diol and DMC (one shot process), in an amount to get a molecular weight around 2000 g/ mol, led to polycarbonates with heterogeneous chain-ends. Indeed, residual methylcarbonate chain-ends were observed in this case. On the other hand, the process of two reactions of 6 h led to product without detectable amounts of methyl groups.

The total conversion of methyl carbonate was first evidenced by NMR spectroscopy. Indeed, the peaks corresponding to the methyl carbonate groups at 3.77 ppm in ¹H NMR spectrum (Fig. 3) and at 155 ppm in ¹³C NMR spectrum, have totally disappeared. Unlike alkyne chain-ends, the phenol and alkene chain-ends exhibited well distinguished NMR signals allowing \overline{Mn} calculations. Moreover, FTIR showed also the disappearance of the band at 1445 cm⁻¹ corresponding to distortion of C–H bonds of the methylcarbonate groups (Fig. 2). The presence of phenol end-groups was also easily



Fig. 4. TGA traces of the prepared telechelic PCs and their polymers.



Fig. 5. FTIR spectra of ADMET polymer, poly(thio-urethane) and HDC polymer.

evidenced by the band at 1515 $\rm cm^{-1}$ arising from aromatic double bonds.

Molecular weights of the functionalized polycarbonates were assessed by SEC and by ¹H NMR using Equation (1). Results are depicted in Table 1. One can observe that *Mn* increased after chainend derivatization. The \overline{Mn} seemed to be affected by the nature of the functional molecule used for derivatization. The more volatile was this molecule, the higher was the \overline{Mn} of the obtained telechelic polycarbonate. Indeed, 9-decen-1-ol (mp = 13 °C and bp = 234-238 °C at atmospheric pressure) and 4-hydroxybenzene ethanol (mp = $89-92 \degree C$ and bp = $190 \degree C$ under 18 mm Hg) did not remove easily at 150 °C under vacuum, unlike 4-hexyn-1-ol, which has a boiling point of 150 °C at atmospheric pressure. Actually, PC4alkene, PC4-phenol and PC4-alkyne exhibited SEC Mn values of 4500, 8900 and 23,100 g/mol, respectively. This result suggests that chain extension occurred independently on the presence of these molecules. To attest this hypothesis, the conditions of chain-end derivatization were applied on PC4-MC alone, in the presence of catalyst (Table 1, PC4-MC control). As expected, an increase of Mn was observed. This result suggested a displacement of a transesterification equilibrated system towards elimination of DMC leading to chain extension.

It is noteworthy that the \overline{Mn} values of linear polycarbonates obtained by SEC evolve linearly with the \overline{Mn} values obtained by ¹H NMR. The equation slope which is called the Benoit Factor [25,26] is of 1.93. In this respect, the absolute \overline{Mn} value of PC4-alkyne, which could not be directly determined by ¹H NMR because of very weak chain-ends signals, could be calculated through the Benoit Factor, i.e. $\overline{Mn} = 11,970$ g/mol ($\overline{Pn} = 52$).

TGA analysis revealed that the new telechelic PCs were more thermally stable than their methylcarbonate terminated precursor (PC4-MC), with regards to temperature values at 5% of degradation (Table 1). The TGA traces of these oligomers are presented in Fig. 4. Furthermore, DSC analysis showed that chain-ends functionalization with phenol and alkyne groups led to slight increase of melting points of the crystalline zones, associated with a slight decrease of the melting enthalpy, suggesting a slight decrease of crystallinity.

3.3. Synthesis and properties of polymers from the prepared telechelic polycarbonates

The reactivity of the polycarbonate end-groups was tested towards polymerization.

PC4-alkene was self-polymerized through ADMET reaction, using ruthenium Hoveyda-Grubbs catalyst (2nd generation). The reaction was performed under neat conditions for 4 h at 80 °C under vacuum. Then, the mixture was dissolved in THF and an excess of ethyl vinyl ether was added to quench the reaction. The ¹H NMR spectrum of the obtained ADMET Polymer (Fig. 3) revealed the disappearance of vinyl group signals at 4.95 and 5.80 ppm and the appearance of a signal at 5.37 ppm arising from ethylenic protons. However, the FTIR spectrums of ADMET Polymer and PC4-alkene were very close (Figs. 2 and 5). The SEC chromatogram of ADMET Polymer compared to those of PC4alkene and PC4-MC is shown in Fig. 6. The \overline{Mn} value of ADMET Polymer was of 11,200 g/mol while the \overline{Mn} value of its precursor PC4-alkene was of 2400 g/mol (Tables 1 and 2). TGA and DSC analysis (Fig. 4, Tables 1 and 2) showed that ADMET Polymer and PC4-alkene have very close thermal properties (Fig. 6).

The phenol terminated polycarbonate (PC4-phenol) was reacted with *p*-phenylene diisothiocyanate, in the presence of DBTL as catalyst, to afford Poly(thio-urethane). THF solutions of the starting mixture were casted in a PTFE mould for 2 h at room temperature under argon atmosphere. The material obtained after solvent evaporation was next cured for 22 h at 60 °C. However, the obtained polymer was not well soluble in common organic



Fig. 6. SEC chromatograms of PC4-MC, PC4-alkene and ADMET polymer.

Table 2 Physico-chemical properties of ADMET polymer, poly(thio-urethane) and HDC polymer.

Polymer code	Precursor	SEC		TGA		DSC ^c					
		Mn	Ð	T _{5%} (°C)	T_{max} (°C)	T _g (°C)	T _m (°C)	$\Delta H_m \left(J/g \right)$	$T_{c}(^{\circ}C)$	$\Delta H_{c} \left(J/g \right)$	
ADMET polymer Poly(thio-urethane)	PC4-alkene PC4-phenol	11,200 /ª	1.8 /ª	305 270	372 349	/b /b	61 62	106 87	49 48	89 90	
HDC polymer	PC4-alkyne	/ ^a	/ ^a	319	369	/ ^D	67	76	53	77	

^a Polymer was not well soluble in SEC solvents.

^b Tg was not observed.

^c Data from second cycle.

solvents for SEC and NMR analysis. On the other hand, the FTIR analysis showed the total disappearance of the isothiocyanate band at 2090 cm⁻¹, and the appearance of supplemental aromatic bands at 1550 and 852 cm^{-1} ascribed to the reacted *p*-phenylene diisothiocvanate. The valence vibration band of N–H bond of the thio-urethane function was observed at 3447 cm⁻¹, whereas the carbonyl band of thio-urethane function was overlapped with the carbonyl band of carbonate function at 1736 cm⁻¹. TGA analysis showed that Poly(thio-urethane) was less thermally stable than its precursor PC4-phenol (Fig. 4). Actually, T_{5%} of Poly(thiourethane) was of 270 °C against 326 °C for PC4-phenol (Tables 1 and 2). This is due to the fragility of the thio-urethane function comparing to the carbonate one. Furthermore, because *p*-phenylene diisothiocyanate is present in Poly(thio-urethane) at only 4 wt%, the melting and crytallization temperatures of this polymer are those of the polycarbonate segment, i.e. close to those of PC4-phenol.

Finally, the reactivity of alkyne end-groups of PC4-alkyne was studied towards the Cu^l-catalysed Huisgen 1,3-dipolar cycloaddition (HDC) with 1,12-diazidododecane. 1,12-diazidododecane was prepared through a classical pathway consisting in the reaction of mesyl chloride with 1,12-dodecanediol, and then the displacement of the mesylate groups with sodium azide in organic medium. The polymerization reaction by HDC was conducted at 50 °C for 24 h in THF medium, in presence of the mixture CuSO₄/sodium ascorbate as catalyst. It is noteworthy that the HDC Polymer started to precipitate in the medium after only 4 h of reaction. HDC Polymer was also not well soluble in common organic solvents for NMR and SEC analysis. The FTIR spectrum of HDC Polymer showed mainly the disappearance of the band of the azide group at 2100 cm⁻¹. Moreover, because of HDC Polymer is based on only 2 wt% of 1,12-diazidododecane, their thermal properties (Fig. 4, Tables 1 and 2) were very close to those of the polycarbonate chains (PC4-alkyne).

4. Conclusion

Telechelic polycarbonates were successfully synthesized by a two-step organocatalytic process. Oligocarbonates with alkyne, alkene and phenol end-groups were prepared as examples. The reactivity of these end-groups towards some polymerization reactions, i.e. the click HDC, ADMET and polycondensation, was evidenced. This process could be used to prepare a range of new versatile telechelic polycarbonates that can be used as precursors of technical and engineering polymers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.04.046.

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